

## Copper(II) Sulfate Dehydration of Alcohols

GEORGE W. FRANCIS and JARLE F. BERG

Department of Chemistry, University of Bergen,  
N-5014 Bergen-Univ., Norway

Methods for the dehydration of alcohols to alkenes are legion, but the single step procedures mostly suffer from the disadvantage of double bond migration.<sup>1,2</sup> It is reported in the literature that anhydrous copper(II) sulfate may be used for the heterogeneous dehydration of secondary and tertiary alcohols in the liquid phase without this drawback.<sup>3-7</sup> In view of the limited data available and the fact that the method has not been much applied, we have undertaken a reinvestigation.

The literature procedure consists of the slow addition of the alcohol to the anhydrous salt at about 190 °C, such that the alkene is distilled off as formed.<sup>3-5</sup> The method as described requires that the temperatures chosen lie between the boiling points of the alkene and alcohol. Since copper(II) sulfate begins to decompose at temperatures not much in excess of 200 °C, the procedure has obvious limitations. The present work circumvented these difficulties by carrying out the reaction in a sealed tube.

Initial experiments were carried out to establish a standard procedure and these showed that satisfactory conversion required temperatures of not less than 180 °C and a reaction period of 24 h. Lower temperatures or shorter reaction times led to increased recoveries of unchanged alcohol. Equal weights of alcohol and anhydrous copper(II) sulfate were used throughout.

On completion of the reaction period the organic products were recovered by partition between water and ether. After drying and removal of ether, total recovery was confirmed and the crude product examined by GC-MS. When a main product was present, this was isolated by microdistillation or recrystallisation and characterised by IR, NMR and MS. The alcohols investigated together with the products of the reactions are given in Table 1.

The two tertiary alcohols (1-2) investigated provided the corresponding alkenes in excellent yields with only small amounts of unidentified products. Distillation gave pure alkenes whose identities were confirmed by IR, NMR and MS.<sup>8,9</sup>

The expected alkene was obtained in about 90 % yield from treatment of each linear secondary alcohol (3-6). The alkenes as obtained were contaminated by about 5 % of the corresponding dialkyl ether and were freed from this contamination by microdistillation under reduced pressure. The *trans*-alkene was isolated by way of the corresponding urea complex.<sup>10</sup> In each case the *cis/trans* ratio was about 1/3. GC-MS on a SCOT-column failed to reveal the presence of alkenes with shifted double bonds. Subsequent studies, involving chemical transformations, confirmed this finding.<sup>11,12</sup> The identity of 7-pentadecene was further confirmed by direct comparison with the authentic compound prepared by Wittig reaction.<sup>11,12</sup> Each *trans*-alkene gave satisfactory IR, NMR and MS data.<sup>8,9</sup>

The cyclic secondary alcohols (7-8) yielded complicated product mixtures where the cycloalkenes derived by 1,2-dehydration were the main products. However, the ether derived from the alcohol represented a significant by-product. The less sterically hindered alcohol (8) provided the larger quantity of ether,

Table 1. The products of the copper(II) sulfate dehydration of the alcohols (1-12).

Alcohol	Products (per cent)		
	Alkene	Ether	Unidentified
4-Propyl-4-heptanol (1)	88 <sup>d</sup>	—	12
5-Butyl-5-nonanol (2)	92 <sup>d</sup>	—	8
6-Undecanol (3)	86 <sup>d</sup>	8	6
7-Tridecanol (4)	88 <sup>d</sup>	10	2
8-Pentadecanol (5)	91 <sup>d</sup>	6	3
9-Heptadecanol (6)	89 <sup>d</sup>	6	5
2-Methylcyclohexanol (7)	45 <sup>a</sup> ; 26 <sup>b</sup>	14	15
3-Methylcyclohexanol (8)	7 <sup>b</sup> ; 48 <sup>c</sup>	38	7
1-Dodecanol (9)	5	90 <sup>d</sup>	5
1-Tridecanol (10)	5	94 <sup>d</sup>	1
1-Pentadecanol (11)	5	90 <sup>d</sup>	—
2-Phenylethanol (12)	—	94 <sup>d</sup>	6

<sup>a</sup> 1-Methylcyclohexene. <sup>b</sup> 3-Methylcyclohexene. <sup>c</sup> 4-Methylcyclohexene. <sup>d</sup> Isolated product gave satisfactory spectral data.

although the significance of this is unclear. The cyclohexenes were identified by comparison of their MS with the literature.<sup>14</sup>

The primary alcohols (9–12) all provided in excess of 90% yields of the appropriate ether. About 5% of alkene was present in most cases, together with a range of unidentified minor products. The aliphatic ethers were purified by recrystallisation from methanol, while diphenethyl ether was distilled. IR, NMR and MS data obtained for the ethers accorded with expectation.<sup>15</sup>

The above results show that the method now described is suitable for the preparation of alkenes from tertiary and secondary acyclic alcohols. A simple alternative synthesis of ethers derived from primary alcohols is also demonstrated. Cyclic secondary alcohols provide a mixture of products and in these cases the reaction is not immediately predictable.

Supplementary experiments carried out with reduced amounts of copper(II) sulfate indicate that 0.5 molar quantities of the salt are required for satisfactory alkene synthesis from tertiary and secondary alcohols. Only 0.05 molar quantities of salt are needed for ether synthesis from primary alcohols. Pilot experiments with other transition metal sulfates and copper salts indicate that these cannot replace copper(II) sulfate in the alkene synthesis. The use of metal salts in liquid phase dehydration is largely unstudied,<sup>1,2</sup> and the mechanisms involved are unclear. Further work on the utility and mechanism of the reaction is in progress.

**Experimental.** The compounds 1–6 were prepared by standard Grignard procedures<sup>16</sup> and gave satisfactory physical data. Compounds 7–12 were commercial products (*purum* grade) from Fluka AG, Switzerland. Urea (*puriss.* grade) was obtained from the same firm. Copper(II) sulfate pentahydrate (*pro analysi* grade), Merck, Germany, was dried at 180°C prior to use in order to remove all water of crystallisation.

Spectroscopic data were checked on a Unicam SP 200G infrared spectrometer, a JEOL C-60H NMR spectrometer, and a JEOL JMS D-100 mass spectrometer coupled to a JGC-20K gas chromatograph. Gas chromatography was accomplished using a commercially-available SE-30 SCOT-column obtained from SGE Pty. Ltd., Australia and guaranteed to have a NEFF-value in excess of 20 000.

**Dehydration procedure.** Anhydrous copper(II) sulfate (*ca.* 1 g) was sealed in a pyrex vial with an equal weight of the alcohol to be investigated. The vial was then maintained at 190°C for 24 h. The vial was allowed to cool and then opened. The contents were shaken with a mixture of water (100 ml) and ether (50 ml). After separation the water layer was extracted with further portions of ether (2 × 50 ml), dried over anhydrous sodium sulfate, and the ether removed under reduced pressure. The total recovery was then found, quantitative in all

cases, and the crude product examined by IR and GC-MS. Product distribution was determined on the basis of the total ion current trace from the GC-MS recorder.

**trans-Alkenes.**<sup>10</sup> The *cis/trans* alkene (*ca.* 1 g) was shaken for 24 h with a saturated solution of urea in methanol (20 ml). The resultant crystals were washed twice with small portions of saturated urea-methanol and then decomposed by the addition of water (20 ml). Ether extraction and evaporation under reduced pressure yielded the pure *trans*-alkene which was used to confirm identity spectroscopically.

**Acknowledgement.** We wish to thank the Royal Norwegian Council for Scientific Research (NAVF) and Ing. Arne Reppen for technical assistance.

1. Knözinger, H. In Patai, S., Ed., *The Chemistry of the Hydroxyl Group, Part 2*, Interscience, New York 1971, p. 641 *et seq.*
2. Saunders, W. H. and Cockerill, A. F. *Mechanisms of Elimination Reactions*, Wiley-Interscience, New York 1973, p. 221 *et seq.*
3. Meyer, A. and Tuot, M. *C. R. Acad. Sci. Ser. C* 196 (1933) 1231.
4. Tuot, M. *C. R. Acad. Sci. Ser. C* 197 (1933) 1434.
5. Tuot, M. *C. R. Acad. Sci. Ser. C* 211 (1940) 561.
6. Whitmore, F. C. and Rorhmann, E. *J. Am. Chem. Soc.* 63 (1941) 2033.
7. Schlatter, M. J. *J. Am. Chem. Soc.* 76 (1954) 4952.
8. Stehling, F. C. and Bartz, K. W. *Anal. Chem.* 38 (1966) 1467.
9. Loudon, A. G. and Maccoll, A. In Zabicky, J., Ed., *The Chemistry of Alkenes, Vol. 2*, Interscience, London 1970, p. 327 *et seq.*
10. Schlenk, W. *Justus Liebig's Ann. Chem.* 565 (1949) 204.
11. Francis, G. W. and Veland, K. *To be published.*
12. Francis, G. W. and Tande, T. *J. Chromatogr. In press.*
13. Hauser, C. F., Brooks, T. W., Miles, M. L., Raymond, M. A. and Butler, C. B. *J. Org. Chem.* 28 (1963) 372.
14. Budzikiewicz, H., Brauman, J. I. and Djerassi, C. *Tetrahedron* 21 (1965) 1855.
15. Spittler-Friedmann, M. and Spittler, G. *Chem. Ber.* 100 (1967) 79.
16. Ongley, P. A., Ed., *Organicum*, Pergamon, Oxford 1973, p. 524 *et seq.*

Received June 27, 1977.